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NUMBER 5

HUMIDITY DATA EXPRESSED IN GRAINS WATER VAPOUR PER POUND OF DRY AIR¹

BY EDGAR STANSFIELD²

Abstract

For some purposes humidity is best stated as weight of water vapour admixed with unit weight of dry air, but this information cannot be found in the ordinary psychrometric tables. Tables and charts are here given relating the air temperature, the depression of the wet bulb thermometer of the sling psychrometer, and the barometric pressure with the humidity in grains of water vapour per pound of dry air. The A.S.T.M. specifications for knock characteristics of motor fuels designate minimum and maximum limits of humidity for the air supplied to the engine. The depressions of the wet bulb thermometer corresponding to these limits are shown in one figure.

The specification of the American Society for Testing Materials for "Knock Characteristics of Motor Fuels", D 357-42 T, requires that in the determination of octane ratings of gasoline the air supplied to the engine shall contain not less than 25 nor more than 50 grains of water vapour per pound of dry air. These data are not given in the ordinary psychrometric tables. Two types of charts have been prepared for use in the laboratory. Examples are shown below.

Fig. 1 shows for five barometric pressures, 26 in. to 30 in., and for air temperatures ranging from 60° to 90° F., the depression of the wet bulb thermometer of the sling psychrometer corresponding to 25 grains water vapour, and to 50 grains water vapour, per pound of dry air. These curves can be used to ascertain whether any wet and dry bulb thermometer readings do or do not indicate humidities within the specified limits; but they cannot be used for giving accurate readings of humidity. The necessary calculations are notably tedious, but Table I gives values that can be used to plot these curves on any desired scale.

Fig. 2 shows for one barometric pressure, 30 in., and for seven air temperatures, 60°, 65°, 90° F., the grains of water vapour per pound of dry air corresponding to any depression of the wet bulb thermometer of the sling psychrometer, from 0° to 35° F.

¹ Manuscript received March 9, 1943.

Contribution from the Research Council of Alberta, University of Alberta, Edmonton, Alta.

² Chief Research Engineer.

Separate sets of curves similar to Fig. 2 are required for different barometric pressures. Table II gives values for use in plotting these sets of curves for five barometric pressures, 26, 27, 30 in.

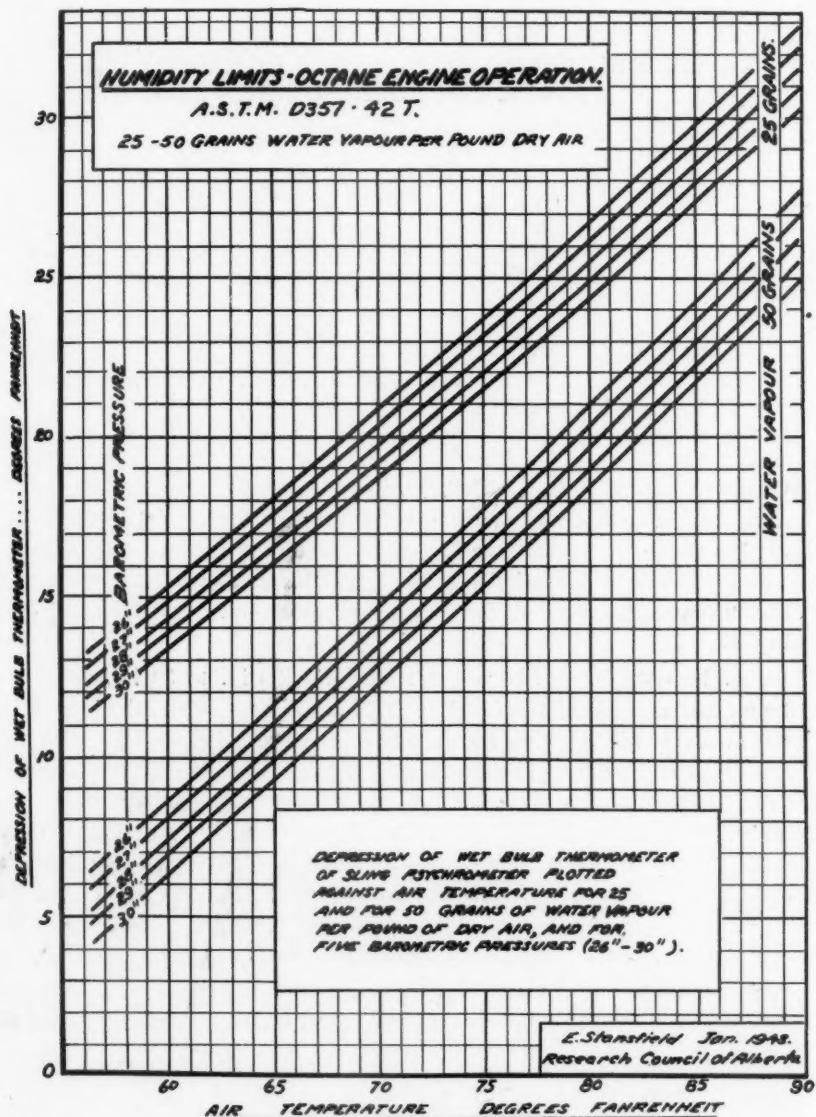


FIG. 1.

The calculations were based on data taken from Psychrometric Tables, W.B. 235, U.S. Bureau of Agriculture, 1937. The density of air was taken as 0.08071 lb. per cu. ft. at 32° F. and 29.92 in. (latitude 45°)—Rayleigh.

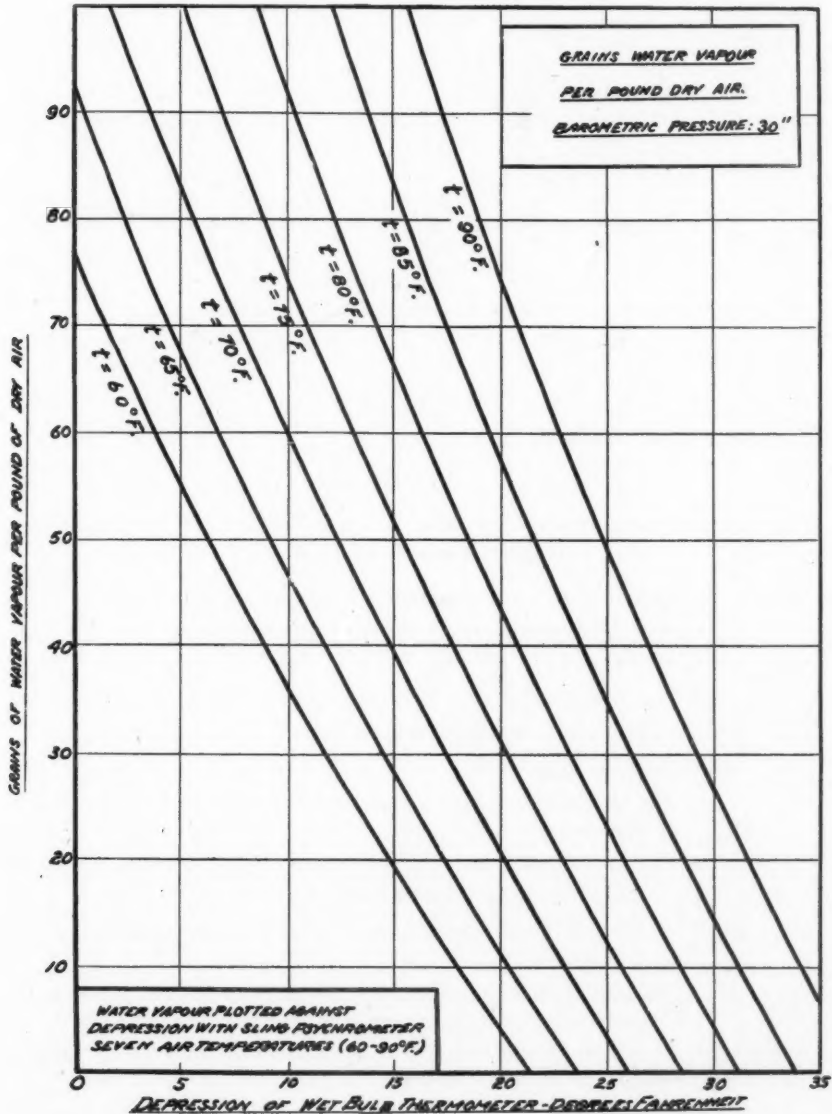


FIG. 2.

TABLE I

DEPRESSION OF WET BULB THERMOMETER, IN DEGREES FAHRENHEIT, FOR 25, AND FOR 50. GRAINS WATER VAPOUR PER POUND OF DRY AIR

t	$P = 30$ in.	$P = 29$ in.	$P = 28$ in.	$P = 27$ in.	$P = 26$ in.	t	$P = 30$ in.	$P = 29$ in.	$P = 28$ in.	$P = 27$ in.	$P = 26$ in.
25 Grains						50 Grains					
60° F.	13.3	13.8	14.3	14.8	15.3	60° F.	6.3	6.9	7.4	8.0	8.6
65	15.9	16.4	16.9	17.5	18.0	65	9.2	9.8	10.4	11.0	11.6
70	18.6	19.2	19.7	20.3	20.8	70	12.3	12.9	13.5	14.1	14.7
75	21.5	22.1	22.6	23.2	23.8	75	15.3	15.9	16.5	17.2	17.8
80	24.4	25.0	25.5	26.1	26.7	80	18.4	19.0	19.7	20.3	21.0
85	27.3	27.9	28.5	29.2	29.8	85	21.6	22.2	22.9	23.6	24.3
90	30.3	30.9	31.6	32.3	32.9	90	24.8	25.5	26.2	26.9	27.6

The equations employed were as follows:—

$$X = W \times V \quad (1)$$

$$p = s' - 0.000367 P (t - t') \left(1 + \frac{t' - 32}{1571} \right) \quad (2)$$

$$W = 11.7449 \times \frac{p}{1 + 0.002037 (t - 32)} \quad (3)$$

$$V = \frac{1}{0.08071} \left(\frac{460 + t}{460 + 32} \right) \left(\frac{29.92}{P - p} \right) \quad (4)$$

where X = weight of water per pound of dry air;

t = dry bulb temperature of sling psychrometer, i.e., air temperature;

t' = wet bulb temperature of sling psychrometer;

$t - t'$ = depression of wet bulb thermometer;

P = barometric pressure;

s' = the maximum or saturation pressure of water vapour at temperature t' ;

p = the actual pressure of water vapour under conditions represented by temperatures t and t' ;

W = weight of water vapour, per cubic foot, at pressure p and temperature t ;

V = volume of one pound of dry air at barometric pressure P , under conditions represented by temperatures t and t' ,

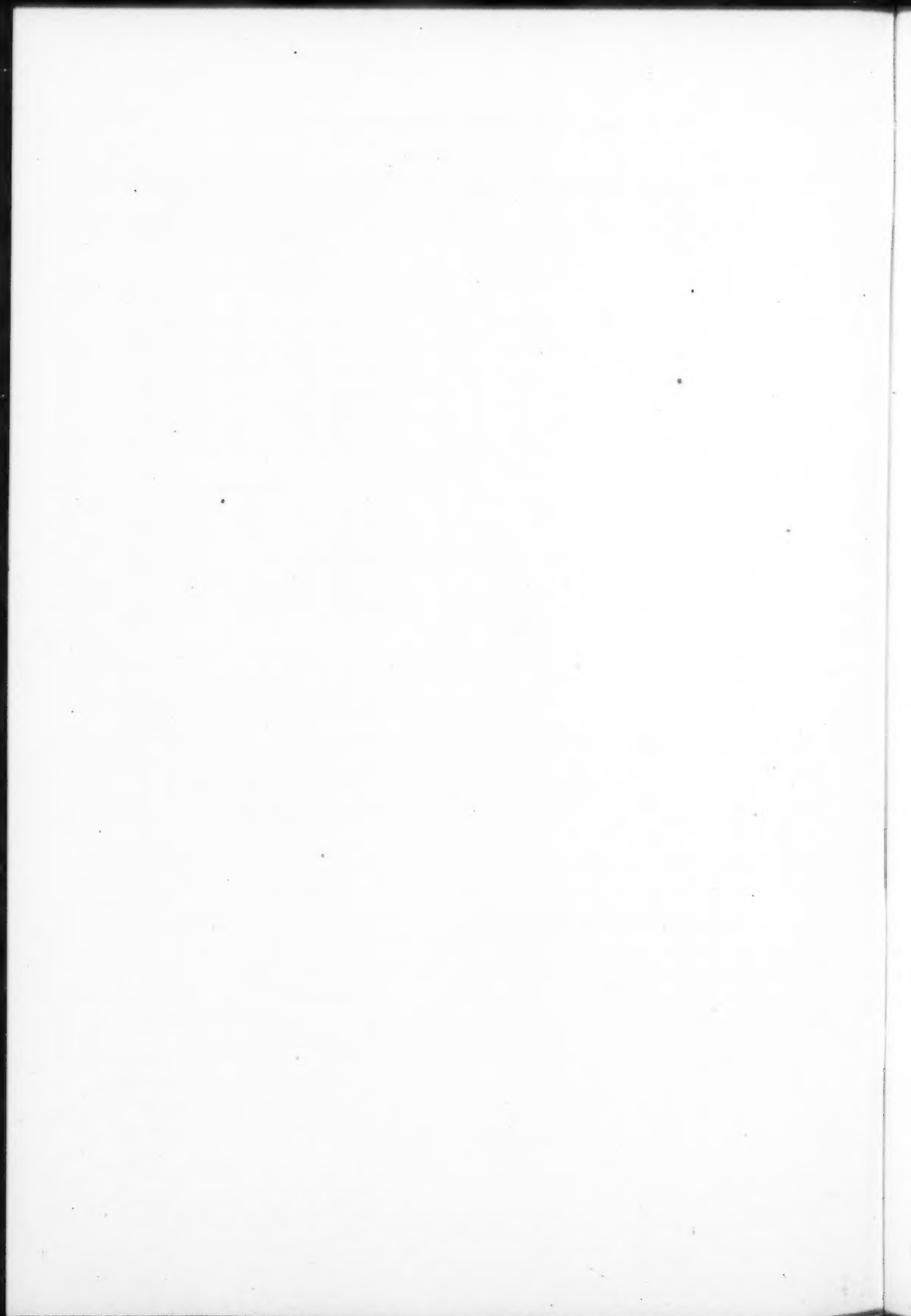
when weights of water vapour are given in grains, temperatures in degrees Fahrenheit, pressures in inches of mercury, and volumes in cubic feet.

Values of s' and Equation (2) were taken from W.B. 235. Equation (3) was taken from same source, with slight modification.

TABLE II

GRAINS OF WATER VAPOUR PER POUND OF DRY AIR FOR DIFFERENT DEPRESSIONS OF WET BULB THERMOMETER, FOR SEVEN AIR TEMPERATURES, AND FIVE BAROMETRIC PRESSURES

$t - t'$	$P = 30$ in.	$P = 29$ in.	$P = 28$ in.	$P = 27$ in.	$P = 26$ in.	$t - t'$	$P = 30$ in.	$P = 29$ in.	$P = 28$ in.	$P = 27$ in.	$P = 26$ in.
$t = 60^{\circ} \text{F.}$						$t = 65^{\circ} \text{F.}$					
1	72.0	74.5	77.4	80.3	83.5	3	77.0	79.8	83.0	86.3	89.9
4	59.3	61.7	64.1	66.8	69.6	6	63.3	66.1	68.9	71.9	75.1
7	47.5	49.7	51.8	54.2	56.6	9	50.9	53.3	55.8	58.3	61.1
10	36.4	38.2	40.2	42.3	44.5	12	39.2	41.4	43.5	46.0	48.4
13	26.0	27.5	29.3	31.2	33.2	15	28.2	30.1	31.9	34.1	36.3
16	15.9	17.3	18.9	20.6	22.4	18	17.8	19.5	21.1	23.0	25.1
19	6.7	8.0	9.4	10.8	12.3	21	7.8	9.3	10.9	12.4	14.3
22	—	—	0.2	1.4	2.9	24	—	—	1.2	2.7	4.4
$t = 70^{\circ} \text{F.}$						$t = 75^{\circ} \text{F.}$					
2	98.1	101.7	—	—	—	7	89.6	93.2	97.0	101.1	105.6
5	82.8	86.0	89.5	93.1	97.1	10	74.4	77.5	80.9	84.7	88.6
8	68.5	71.4	74.5	77.8	81.4	13	60.2	63.0	66.1	69.5	73.0
11	55.3	57.8	60.5	63.5	66.7	16	46.9	49.5	52.2	55.2	58.4
14	42.8	45.1	47.5	50.1	52.9	19	34.5	36.8	39.2	41.8	44.5
17	31.0	33.1	35.3	37.6	40.2	22	22.9	24.9	27.0	29.4	31.9
20	20.0	21.9	23.8	26.0	28.1	25	11.9	13.7	15.6	17.6	20.0
23	9.6	11.3	12.9	14.9	16.8	28	1.6	3.2	5.0	6.8	8.7
26	—	1.2	2.8	4.4	6.2						
$t = 80^{\circ} \text{F.}$						$t = 85^{\circ} \text{F.}$					
9	97.2	101.2	105.5	110.1	115.0	14	88.7	92.6	97.1	101.5	106.3
12	81.2	84.6	88.5	92.5	96.5	17	72.7	76.2	80.0	84.1	88.5
15	65.9	69.1	72.6	76.1	80.1	20	57.5	60.7	64.1	67.8	71.6
18	51.8	54.7	57.7	61.0	64.6	23	43.5	46.4	49.4	52.7	56.1
21	38.6	41.2	43.8	46.8	50.0	26	30.4	33.0	35.6	38.6	41.8
24	26.3	28.6	31.0	33.6	36.5	29	18.1	20.4	22.7	25.3	28.1
27	14.7	16.7	18.9	21.2	23.7	32	6.5	8.6	10.7	13.1	15.6
30	3.8	5.6	7.5	9.5	11.8	35	—	—	—	1.4	3.7
33	—	—	—	—	0.7						
$t = 90^{\circ} \text{F.}$											
16	97.4	101.8	106.5	111.6	117.1						
19	80.3	84.1	88.4	92.8	97.5						
22	64.2	67.7	71.6	75.6	80.0						
25	49.2	52.2	55.7	59.3	63.2						
28	35.2	38.0	41.1	44.3	47.9						
31	22.2	24.6	27.4	30.3	33.4						
34	9.9	12.2	14.5	17.2	20.0						



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USE OF THE HARING CELL FOR MEASURING ADDITION AGENT CONCENTRATION IN ELECTROLYTIC BATHS¹

BY W. GAUVIN² AND C. A. WINKLER³

Abstract

Cathode polarization measurements during electrodeposition from acid copper sulphate solutions were made with a Haring cell, using a method previously developed (4). Measurements made at 2°, 24.8°, and 50.1° C. show that the polarization decreases as temperature increases, this decrease being larger for a temperature change from 2° to 24.8° C. than for a change from 24.8 to 50.1° C. An increase in acidity has little effect on the polarization (except for low acidities) at apparent current densities below 2 amp. per dm.², while it results in an increase in polarization above that value. The increase in polarization caused by various concentrations of gelatin was studied at -4.2°, 2°, 24.8°, and 50.1° C. For a given gelatin concentration, the increase in polarization is greater the lower the temperature, while for a given temperature, the relative increase in cathode polarization is greater at smaller gelatin concentration. It is concluded that control of the gelatin or glue concentration of an electrolyte with a Haring cell may be considerably improved by making the measurements at low temperatures and in dilute solutions.

Introduction

A definite relation has been stated by Haring (7) to exist between cathode polarization and the concentration of glue used as addition agent in the electrodeposition of copper. The Haring cell was used subsequently by many investigators to make cathode polarization measurements, but the results recorded in the literature show marked disagreement. The apparent lack of agreement in certain cases might be attributable to failure of the investigators to report fully the conditions under which the measurements were made. Nevertheless, the information available does not seem to substantiate the original claim that use of the cell should enable the operator to maintain close control of the addition agent concentration.

Since the principle of the Haring method appeared to be sound enough, an investigation was made to determine the conditions under which satisfactorily reproducible cathode polarization measurements might be made. The results reported in a previous paper (4) showed that the cathode polarization for carefully controlled conditions of electrolysis were reproducible when sufficient time was permitted for steady state to be attained. On the basis of this information, the present study was made to assess the applicability of the

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Haring cell to the problem of determining the concentration of gelatin used as addition agent in copper electrodeposition. At the same time, a study was made of the effect of temperature and acid concentration on the cathode polarization in presence of gelatin.

Experimental

The electrolytic cell and electrical equipment used were the same as described in the previous paper (4). The gelatin was Eastman purified, with a moisture content of 11.9% on a moist gelatin basis. All weights of the addition agent reported are given on the moist basis. Sulphuric acid and copper sulphate were reagent grade.

Prior to making measurements of the cathode polarization at different apparent current densities, under given conditions of electrolysis, standard surface characteristics were imparted to the cathode by electrolyzing to the steady state polarization value at 26.4° C., with an apparent current density of 2 amp. per dm.² in an electrolyte containing 125 gm. per litre of copper sulphate pentahydrate, and 50 gm. per litre of concentrated sulphuric acid in distilled water (solution No. 17). When the standard base metal surface had been established, the proper amount of electrolyte to be studied was placed in the cell, following the procedure used in the previous investigation, the temperature of the thermostat adjusted to the desired value, and measurements of the cathode polarization were made for a range of apparent current densities beginning with the value 0.2 amp. per dm.² After attainment of the steady state polarization value at this current density, which required a few minutes only, the apparent current density was increased in successive increments of 0.2 amp. per dm.², the polarization being measured after the lapse of five minutes from the time the current was adjusted after each increment. A previous experiment had shown, it is true, that at apparent current densities in the range from approximately 0.5 to 1.0 amp. per dm.², constant polariza-

TABLE I
COMPOSITION AND CONCENTRATION OF ELECTROLYTES

Solution No.	Copper sulphate, gm./litre	Sulphuric acid, gm./litre	Gelatin, mg./litre	Solution No.	Copper sulphate, gm./litre	Sulphuric acid, gm./litre	Gelatin, mg./litre
17	125	50	0	28	125	150	10
18	125	50	1	29	125	0	0
19	125	50	5	30	125	25	0
20	125	50	10	31	125	100	0
21	125	50	100	32	125	225	0
22	125	50	500	33	62.5	150	0
23	125	50	750	34	62.5	150	0.5
24	125	50	1000	35	62.5	150	1
25	125	150	0	36	62.5	150	2.5
26	125	150	1	37	125	150	2
27	125	150	5				

tion values would not be attained after five minutes. Experience soon demonstrated, however, that reproducible relative polarization values, satisfactory for present purposes, could be obtained by this procedure, providing the same standard base metal surface was always used as a starting point.

In Table I are recorded the composition and concentration of the various electrolytes investigated, and also the numbers by which they are designated on the graphs.

Results

Effect of Acid Concentration on Cathode Polarization

Measurements were first made to determine the effect of acidity on the cathode polarization, since there seems to be little agreement among different investigators on this point. It has been reported, for example, that an increase of acidity in copper sulphate baths results in: no effect on the polarization (8); a decrease in the polarization (7); an increase (10); an increase, followed by a decrease (5); and a large initial decrease, followed by steady values at higher acidities (3).

The results of the present study, made at 24.8° C., with electrolytes containing 125 gm. of copper sulphate pentahydrate per litre of solution, are represented graphically in Fig. 1. It was not possible to extend the measurements for the solution containing no acid (No. 29), nor for that containing

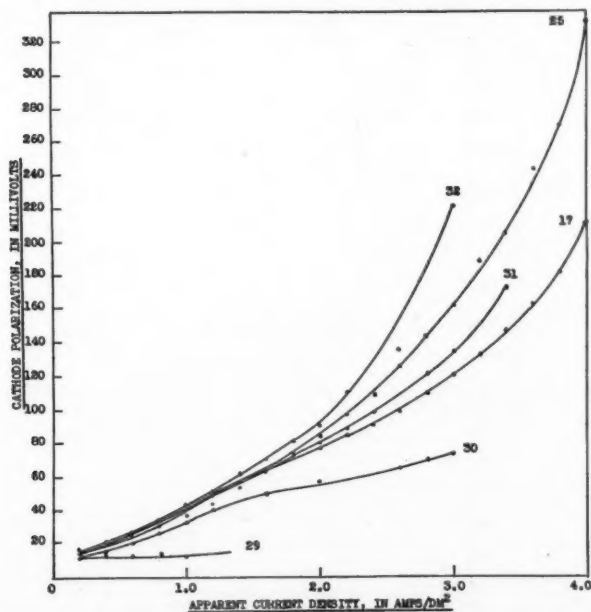


FIG. 1. Effect of acidity on cathode polarization. Temperature, 24.8° C. Initial surface: standard base. Solutions: No. 29, no sulphuric acid; Nos. 30, 17, 31, 25, and 32—25, 50, 100, 150, and 225 gm. per litre of sulphuric acid, respectively.

25 gm. per litre of acid (No. 30), owing to the low conductivities of these solutions, which rendered the current source and potentiometer used unsuitable at higher current densities. At apparent current densities less than 1.0 amp. per dm.², there appears to be a marked increase in polarization with increase of acid concentration up to 50 gm. per litre. Above this concentration, the cathode polarization seems to suffer little change with further increase in acid content of the solution. At higher current densities, the rate at which the polarization increases with increasing apparent current density is generally greater the higher the acid concentration, although there are certain irregularities in the results that do not conform to this generalization. It should not be surprising, perhaps, if a simple relation between cathode polarization and acid content of the solution does not exist, since the acidity of the cathode film appears to be a function of both the acid content of the electrolyte (1) and the apparent current density (9).

Effect of Temperature on Cathode Polarization

It has long been known that an increase of temperature decreases the cathode polarization. However, the nature of this change has never been investigated. The cathode polarization has, therefore, been determined at 2°, 24.8°, and 50.1° C. for a range of apparent current densities, in solution No. 25. The results are shown in Fig. 2. Obviously, the decrease in polariza-

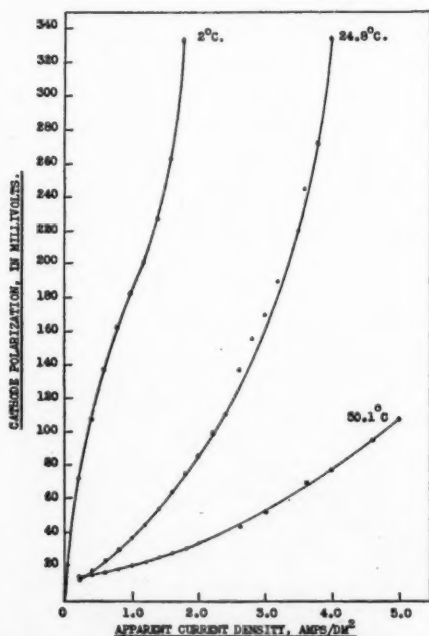


FIG. 2. Effect of temperature on cathode polarization. Solution: No. 25 (all 3 curves). Temperatures: 2°, 24.8°, and 50.1° C. Initial surface: standard base.

tion observed between the 2° and 24.8° curves is much greater than that observed for a temperature change from 24.8° to 50.1° C., at any given current density.

Effect of Gelatin Concentration on Cathode Polarization at 24.8° C. in Weak Acid Electrolyte

Experiments were made to determine the effect of increasing gelatin concentrations on the cathode polarization at 24.8° C., for a wide range of concentrations. The results are shown in Fig. 3. The electrolyte used

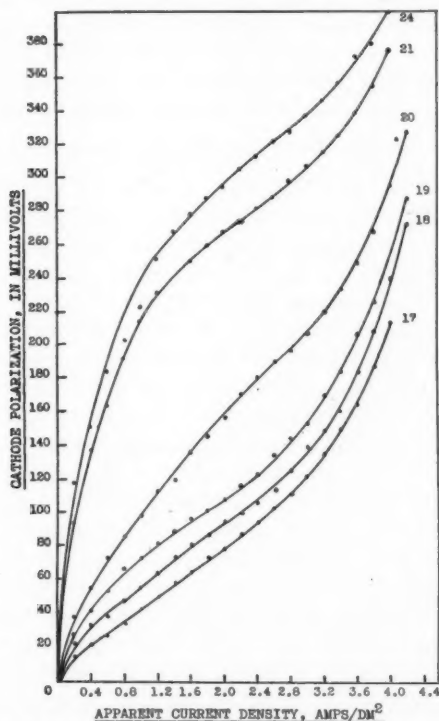


FIG. 3. Effect of gelatin concentration on cathode polarization at 24.8° C. in weak acid electrolytes. Solutions: No. 17, no gelatin; Nos. 18, 19, 20, 21, and 24—1, 5, 10, 100, and 1000 mg. per litre of gelatin, respectively.

contained 125 gm. per litre of copper sulphate pentahydrate and 50 gm. per litre of concentrated sulphuric acid. Each curve of Fig. 3 is the average of five with maximum deviation of ± 3 mv. for apparent current densities below 1.5 amp. per dm.², and ± 4 mv. for apparent current densities between 1.5 and 4 amp. per dm.² Measurements at apparent current densities above the latter value were not reliable, possibly owing to localized attainment on the cathode of the hydrogen overvoltage. This assumption is quite logical, in

view of the evidence recently presented by Read and Graham (9), who showed that the current density is not uniform over the whole immersed area of a cathode, but increased from the bottom to the top of the cathode surface. It has also been shown that polarization values vary somewhat over the face of the cathode (10). In other words, only average values of the polarization for the whole cathode surface can be measured with the Haring cell, but that these average values are reproducible within close limits, when obtained under carefully controlled conditions, is amply shown by the results obtained.

Measurements with 100 and 1000 mg. per litre of gelatin were somewhat less precise than at lower gelatin concentrations, probably as a result of periodicity in the deposition (6). In commercial practice, however, concentrations of glue, expressed in terms of gelatin, rarely exceed 3 to 5 mg. per litre, in which range the polarization measurements are considerably more reliable.

Effect of Gelatin Concentration on Cathode Polarization at Different Temperatures, in Strongly Acid Electrolytes

Commercial electrolytes generally contain concentrations of acid higher than that used in the preceding study. Studies were made, therefore, using electrolyte containing 125 gm. per litre of copper sulphate pentahydrate and 150 gm. per litre of concentrated sulphuric acid. The results obtained at 2°, 24.8°, and 50.1° C. are shown in Fig. 4-A, -B, and -C, respectively. Comparison of Figs. 3 and 4-B shows that the increase in polarization at 24.8° C. with increased gelatin content is not as large for the electrolyte containing 150 gm. of acid per litre. It is also evident that, contrary to a previous report (7), increase of temperature decreased, rather than increased, the effect of a given amount of gelatin on the cathode polarization at a given apparent current density. This effect is readily seen from Fig. 5, in which the increase in cathode polarization due to the addition of various amounts of gelatin at different apparent current densities and temperatures is recorded. At 2° C., the effect of added gelatin was greatest, but limiting current density was soon reached. It is interesting to note that measurements at this low temperature were somewhat more precise than at the higher temperatures, especially at apparent current densities below about 1.6 amp. per dm.²

For a given gelatin concentration, the relation of temperature to cathode polarization is quite analogous to that in the absence of gelatin. Since decrease of temperature corresponds to an increased effect of added gelatin on the polarization at given apparent current density (Fig. 5), it was considered worth while to attempt measurements near the freezing point of the electrolyte. Temperatures were controlled within 0.3° C. by adding dry ice to acetone as the thermostat liquid. Preliminary experiments showed that at a given temperature, the anode polarization increased enormously when a definite value of the current density was attained. This "passivity" was soon traced to the precipitation of copper sulphate on the anode from the anode film. The relation between temperature and apparent current density at which precipitation occurred was determined approximately to be:—

Temp., °C.	-8.2	-6.2	-4.0	-3.8
Apparent current density at which precipitation occurred, amp./dm. ²	0.6	1.0	1.4	1.8

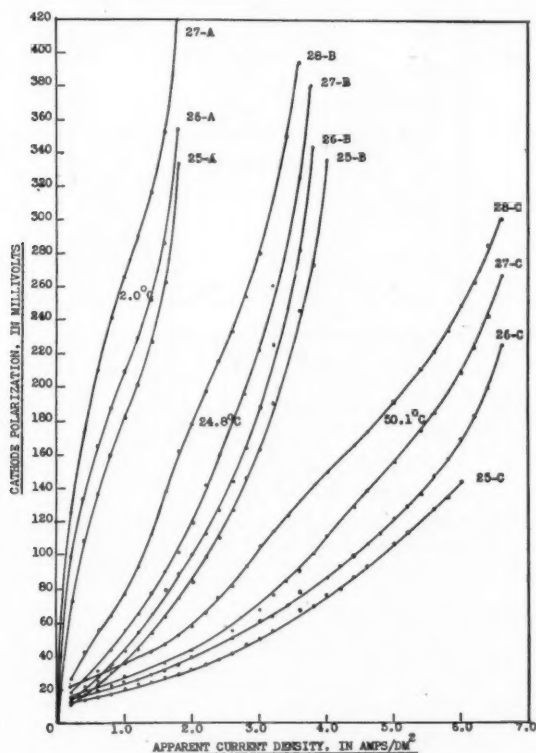


FIG. 4. Effect of gelatin concentration on cathode polarization. Solutions: No. 25, no gelatin; Nos. 26, 27, and 28—1, 5, and 10 mg. per litre of gelatin, respectively. Temperatures: Curves A, 2.0°; Curves B, 24.8°; Curves C, 50.1° C.

This behaviour is interesting in relation to the composition of the anode film, and a more detailed study of it is contemplated.

For purposes of the immediate investigation, difficulties arising from the precipitation of copper sulphate at the anode were circumvented by using an electrolyte containing only half the normal amount of copper sulphate pentahydrate. As the solubility product constant at the anode film temperature was thus not exceeded, no precipitation occurred. The acid content was maintained at 150 gm. per litre, however, in order to have high conductivity, and also to depress the freezing point of the electrolyte (solutions Nos. 33, 34, 35, and 36).

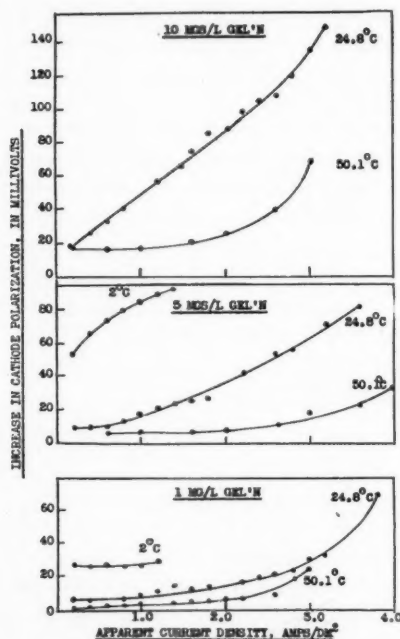


FIG. 5. Increase in cathode polarization due to three concentrations of gelatin, at various current densities and temperatures. Solutions: No. 25, no gelatin, basis of comparison; Nos. 26, 27, and 28—1, 5, and 10 mg. per litre of gelatin, respectively.

Measurements were made at $-4.2^{\circ}\text{C}.$, with the results shown in Fig. 6. Hydrogen evolution invariably occurred at apparent current densities greater than $0.6\text{ amp. per dm.}^2$. This caused fluctuations in the cathode polarization values. It could be observed that during formation of hydrogen bubbles on the cathode, the polarization increased from 5 to 6 mv. above a mean value, followed by a decrease of similar magnitude when a sheet of hydrogen bubbles became detached from the electrode. The plotted polarization values for apparent current densities in excess of $0.6\text{ amp. per dm.}^2$, therefore, must be regarded as approximate only. The values for lower current densities were very reproducible, however, with no fluctuations detectable. The effect of added gelatin on the cathode polarization is more pronounced at the temperature of this experiment than at the higher temperatures used in preceding experiments.

Simultaneously with all cathode polarization measurements, anode polarization determinations were made. It is of interest to note that, although the values of the anode polarization are determined by the temperature, acidity, apparent current density, etc., they are not affected by the addition of gelatin to the electrolyte.

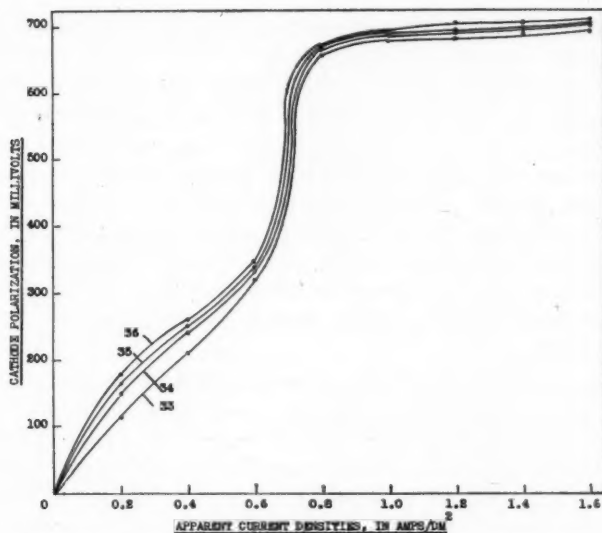


FIG. 6. Effect of gelatin on cathode polarization at -4.2°C . Initial surface: standard base. Solutions: No. 33, no gelatin; Nos. 34, 35, 36—0.5, 1.0, and 2.5 mg. per litre of gelatin, respectively.

Discussion

The main point of interest in the present study was to determine the utility of the Haring cell as an instrument for the determination of addition agent concentration in electrolytic baths. Obviously, it can be useful only when the addition agent produces a change in the cathode polarization. Where such an effect is observed, the accuracy with which addition agent concentration may be determined will, of course, depend upon the magnitude of the change in polarization with given amount of addition agent, as compared with the magnitude of the experimental error. The results that have been presented show that the concentration of gelatin in an electrolytic bath might be determined within 0.4 to 1 mg. per litre, depending upon the temperature used. It must be emphasized, however, that reproducibility of the polarization measurements appears to be contingent upon using a cathode to which standard surface conditions have been imparted (standard base), by electrolyzing in a standard electrolyte under definite conditions, until steady state polarization values are obtained.

From the results presented, it would appear that the sensitivity of the Haring cell as a method of control could be increased in two ways:

- (a) By working at low temperatures,
- (b) By diluting the solution.

Fig. 5, which gives the relative increase in cathode polarization resulting from addition of various amounts of gelatin, clearly shows that at any given

current density and given gelatin concentration, these increments are considerably larger, the lower the temperature.

Figs. 3, 4, 5 and especially 6, all clearly show that the relative increase in cathode polarization due to the addition of a small amount of gelatin to a solution containing none of it is much greater than the increase noted when the same amount of gelatin is added to a solution already containing some of this addition agent. Since the experimental error—which, in the above studies, never exceeded ± 4 mv.—must be taken into account, it is obvious that diluting the solution will bring the concentration of addition agent within a range where its effect on the cathode polarization is considerably greater than the experimental error. This is essentially what was done when making measurements at -4.2°C .

From a commercial point of view, since glue, and not gelatin, is used as the addition agent, it would be necessary to redetermine the relations between cathode polarization and current density in terms of increasing concentrations of glue, and these may differ slightly from those reported for gelatin. It is quite possible that these relations may even vary for glues of different origin. It is interesting to note that slight variations in the nickel, arsenic, iron, and chlorine content of a commercial electrolyte should not affect the cathode polarization determination, since it has been shown that small changes in their concentration have virtually no effect on the polarization (10).

Another point of interest arising from the present study concerns the shape and equation of the polarization curves. It was observed that the curve representing the logarithm of $(P - K_1)$ vs. the logarithm of the logarithm of D , where P is the cathode polarization, D is the apparent current density, and K_1 is a constant, was linear over a considerable range of current densities; this applied to all polarization curves, whether gelatin was present or not. Allowing for the fact that the method followed did not permit attainment of steady state polarization values within the time allotted, for a very few points of the polarization curves in the lower current density range, the range of linearity was noted to extend for Fig. 3, from 0.6 to 3 amp. per dm^2 ; for Fig. 4-A, from 0.2 to 1.2 amp. per dm^2 ; for Fig. 4-B, from 0.2 to 2.4 amp. per dm^2 ; for Fig. 4-C, from 0.2 to 5 amp. per dm^2 ; and for Fig. 6, from 0.2 to 0.6 amp. per dm^2 . Over these ranges, the equation of the polarization curves conformed to the expression

$$P = K_1 + K_2(\log D)^n,$$

where K_2 and n are additional constants.

Volmer showed that for the metals, zinc, cadmium, nickel, lead, bismuth, copper, and silver, there was a linear relation between cathode polarization and current density, for very small values of the latter. From this relation, Volmer concluded that the rate at which the layers of metal spread from the corners and edges of a crystal over its faces was the determining factor in the over-all deposition process (2). It can be assumed, therefore, that, if allowance is made for the presence of concentration polarization in the polarization

values determined with the Haring cell, at some point between a very low value of the apparent current density and the value 0.2 amp. per dm.², a change in one of the deposition processes takes place, following which the two-dimensional growth of the nuclei postulated by Volmer is no longer the rate-determining factor.

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THE ALKALOIDS OF *LYCOPODIUM* SPECIES

III. *LYCOPODIUM ANNOTINUM* L.¹

BY RICHARD H. F. MANSKE² AND LÉO MARION²

Abstract

Eight alkaloids have been isolated from *Lycopodium annotinum* L. Two of these, lycopodine and obscurine, had been described previously. The remaining six bases appear to be new. They are annotinine (L7) ($C_{16}H_{21}O_3N$), alkaloid L8 ($C_{16}H_{20}O_3N$), alkaloid L9 ($C_{16}H_{20}O_3N$), alkaloid L10 ($C_{16}H_{27}ON$), alkaloid L11 ($C_{16}H_{21}O_3N$), and alkaloid L12 ($C_{18}H_{25}O_3N$).

In a previous communication the authors (1) announced that they had examined a number of *Lycopodium* species. An investigation of the alkaloids of *Lycopodium annotinum* L. is now reported. Eight alkaloids have been isolated but only two of these, lycopodine and obscurine (L6), have been found in other species. The chief alkaloid is not lycopodine, of which indeed only a very small quantity was found, but an alkaloid now termed annotinine (L7), best represented by $C_{16}H_{21}O_3N$. It is a lactonic base since it yields a water soluble salt when heated with alcoholic alkali. The base regenerated by heating the acidified solution and adding ammonia is not annotinine but one containing an added molecule of water.

The remaining alkaloids were present to the extent of less than 0.01% and their complete characterization and chemical study are left in abeyance until more is known about the more accessible alkaloids. They are alkaloid L8 ($C_{16}H_{20}O_3N$), alkaloid L9 ($C_{16}H_{20}O_3N$), alkaloid L10 ($C_{16}H_{27}ON$), alkaloid L11 ($C_{16}H_{21}O_3N$, isomeric with annotinine), and alkaloid L12 ($C_{18}H_{25}O_3N$). It should be noted that alkaloid L9 is probably a mixture but, owing to its exceptional behaviour, it has been deemed advisable to retain one designation only until more can be ascertained concerning its nature. Even a cursory survey of the empirical formulae of these alkaloids (with the possible exception of L9, see experimental part) discloses a relation that can hardly be fortuitous. All are C_{16} compounds except alkaloid L12, which presents a similarity to some of the alkaloids of *L. complanatum*, which, with two exceptions, contain 18 carbon atoms. It is for this reason that the purity of the bases eventually obtained from alkaloid L9 is considered doubtful.

It is unlikely that other bases are present in more than the merest traces, although small amounts of material of doubtful homogeneity were isolated. There remained only a small portion of uncrystallized material.

Experimental

There was available a total of 103 kg. of dried material collected in July and August. The entire lot was worked up in the manner already described

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except that chloroform was used to extract the bases referred to as "crude alkaloid" (1).

Annotinine (L7)

The crude alkaloid was redissolved in dilute hydrochloric acid and the filtered solution extracted with chloroform until nothing further was removed (Chloroform extract, -C). The turbid aqueous solution was filtered (charcoal), basified with ammonia, and exhausted with chloroform. The solvent was largely evaporated and hot ethanol added to the partly crystallized residue. The base that then separated was filtered off and washed with methanol in which it is only sparingly soluble. It melted at 230° C.* and when recrystallized from chloroform-methanol annotinine was obtained in brilliant colourless prisms melting sharply at 232° C. Found: C, 69.73, 70.02; H, 7.77, 7.82; N, 5.22, 4.92%. Calc. for $C_{16}H_{21}O_3N$: C, 69.82; H, 7.64; N, 5.09%.

The perchlorate was recrystallized from hot water; it melted at 267° C. Found: C, 51.00, 51.16; H, 6.03, 5.87; N, 3.61%. Calc. for $C_{16}H_{21}O_3N \cdot HClO_4$: C, 51.13; H, 5.86; N, 3.73%.

The total yield of annotinine, including that obtained from the mother liquors, was 87 gm.

Obscurine (L6)

The filtrate from the annotinine was concentrated somewhat. The base which then separated proved to be a mixture of annotinine and obscurine. A portion of the latter was obtained pure by taking advantage of its sparing solubility in chloroform but the annotinine was not obtained pure by direct crystallization. Annotinine perchlorate is virtually insoluble in methanol, whereas obscurine perchlorate is readily soluble and the bases were easily separated in a pure state as the perchlorates. There was obtained a total of 9 gm. of pure obscurine melting sharply at 282° C. either alone or in admixture with a specimen from *L. obscurum*.

Alkaloid L11

The mother liquor from which the annotinine and obscurine had crystallized was evaporated somewhat and neutralized with perchloric acid. The mixture was then completely evaporated *in vacuo* and the residue dissolved in 500 cc. of acetone-ethyl-acetate (1:1). The sparingly soluble perchlorate that then separated proved to be a mixture of that of annotinine and of that of alkaloid L11. The free bases were regenerated and the annotinine crystallized from methanol. The methanolic filtrate from the annotinine was evaporated somewhat. It then deposited large colourless hexagonal crystals, which, after washing with ether, melted indefinitely at 162° C. Further recrystallization from methanol ultimately yielded brilliantly colourless rhombs melting sharply at 174° C. Found: C, 69.69; H, 7.57; N, 5.28%. Calc. for $C_{16}H_{21}O_3N$: C, 69.82; H, 7.64; N, 5.09%.

* Melting points are corrected.

The perchlorate of alkaloid L11 was recrystallized twice from hot water, in which it is moderately soluble. It melts at 239° C. Found: C, 51.13, 51.27; H, 5.99, 6.18; N, 3.68%. Calc. for $C_{16}H_{21}O_3N \cdot HClO_4$: C, 51.13; H, 5.86; N, 3.73%.

Alkaloid L8

The acetone-ethyl-acetate filtrate from which the perchlorates of annotine and alkaloid L11 had separated was diluted with water and boiled to expel organic solvents. The filtered aqueous solution was basified with ammonia and extracted with successive portions of ether. The combined and washed extract was evaporated and the residue dehydrated *in vacuo*. Dry ether was then added. In the course of several days a mixture of obscurine and alkaloid L8 crystallized. It was washed with methanol, which dissolved the latter. The evaporated extract on cooling deposited a crop of pearly plates admixed with a small amount of the needles of obscurine. Repeated extraction with dry ether removed the former and recrystallization from methanol-ether yielded alkaloid L8 in brilliant pearly plates that melted sharply at 180° C. Found: C, 73.13, 73.21; H, 9.51, 9.73; N, 5.48, 5.28%. Calc. for $C_{16}H_{25}O_2N$: C, 73.00; H, 9.51; N, 5.32%.

The perchlorate was recrystallized from methanol-ethyl-acetate. It is moderately soluble in methanol and melts at 318° C. with decomposition but not with much previous darkening when placed in the bath at 300° C. Found: C, 53.03, 53.14; H, 7.48, 7.24; N, 3.98%. Calc. for $C_{16}H_{25}O_2N \cdot HClO_4$: C, 52.82; H, 7.15; N, 3.85%.

Alkaloid L9

The chloroform extract (C) was evaporated and the residue boiled with dilute hydrochloric acid. The filtered (charcoal) extract was exhausted with ether, basified with ammonia, and again exhausted with ether. The combined and washed extract was evaporated and the residue dehydrated *in vacuo*. It was neutralized with perchloric acid in methanol solution and heated on the steam-bath under reduced pressure. The syrupy residue was triturated with successive portions of anhydrous ether until it had largely crystallized. The addition of ethyl acetate made it possible to filter this mixture. The washed perchlorate was extracted with successive portions of acetone (see alkaloid L10). The free base was then regenerated by shaking with ammonia and ether. The residue from the ether solution crystallized readily in contact with hexane with which it was washed. It was then recrystallized twice from dry ether. Alkaloid L9 was thus obtained in stellate aggregates of fine needles melting sharply at 122° C. Found: C, 72.68, 72.82; H, 9.27, 9.28; N, 5.11, 5.19%. Calc. for $C_{16}H_{25}O_2N$: C, 73.00; H, 9.51; N, 5.32%.

The perchlorate was recrystallized from methanol-ethyl-acetate and consisted of brilliant colourless plates melting with effervescence at 209°. Found: C, 54.48; H, 7.65% (average of four determinations); N, 3.46% (average

of three determinations). Calc. for $C_{19}H_{31}O_3N \cdot HClO_4$: C, 54.10; H, 7.59; N, 3.32%.

Owing to the discrepancy between the analytical figures obtained for the base and those obtained for the perchlorate, the latter was recrystallized from methanol instead of the mixture of methanol and ethyl acetate. It was obtained in colourless needles melting at 267° which, in admixture with annotinine perchlorate, had completely melted at 255° . Found: C, 55.01, 55.08; H, 7.51, 7.56; N, 3.93%.

The base, melting sharply at 122° , was dissolved in ethyl acetate containing a little acetone and the solution neutralized with perchloric acid. The crystalline perchlorate was recrystallized from methanol. The crystalline deposit consisted of clear plates mixed with aggregates of needles, which were separated mechanically and purified by fractional crystallization, the plates being slightly less soluble in methanol than the needles. The first perchlorate was obtained as brilliant, triangular plates melting at 273.5° . Found: C, 53.19, 53.32; H, 6.98, 7.03; N, 3.41, 3.36%. Calc. for $C_{20}H_{31}O_3N \cdot HClO_4$: C, 53.39; H, 7.12; N, 3.12%.

A small quantity of this perchlorate was dissolved in hot methanol and the solution basified with ammonia. The base was extracted with ether, the combined extract dried over sodium hydroxide pellets and the solvent distilled off. The oily residue was distilled *in vacuo* (b.p. 150 to 153° (0.5 mm.)) and dissolved in warm hexane, from which it crystallized on cooling. After several recrystallizations from this solvent, the base was obtained in aggregates of colourless prisms melting at 98° . In admixture with alkaloid L2 (m.p. 97°) (1) it was completely liquid at 70° . Found: C, 68.77, 68.44; H, 8.53, 8.72; N, 4.03%. Calc. for $C_{20}H_{31}O_4N$: C, 68.77; H, 8.88; N, 4.01%.

The second perchlorate, which crystallized in needles, was recrystallized repeatedly from methanol and finally obtained as stellate aggregates of colourless needles melting at 276° , with previous darkening. Found: C, 55.12, 54.91; H, 7.17, 7.15; N, 3.85, 3.82%. Calc. for $C_{16}H_{23}ON \cdot HClO_4 \cdot 0.5 CH_3OH$: C, 54.78; H, 7.19; N, 3.87%.

Lycopodine

The base from the hexane filtrate from alkaloid L9 was dissolved in acetone and neutralized with perchloric acid. The sparingly soluble perchlorate was recrystallized from hot water. Either alone or in admixture with an authentic specimen of lycopodine perchlorate it melted at $283^\circ C$. The free base was regenerated and recrystallized from hexane. It melted at $116^\circ C$. either alone or admixed with lycopodine. The total yield was 7 gm.

Alkaloid L10

The acetone extract obtained from the perchlorate of alkaloid L9 was evaporated somewhat and the salt that then separated filtered off. The filtrate was evaporated to a small volume and treated with ethyl acetate. The solid perchlorate was still a mixture but by systematically working up the more soluble portion there was ultimately obtained about 1.0 gm. of

colourless short prisms that melted sharply at 223° C. Found: C, 54.74, 54.97; H, 7.39, 7.77; N, 3.80, 3.81%. Calc. for $C_{18}H_{27}ON \cdot HClO_4$: C, 54.93; H, 8.01; N, 4.01%.

Alkaloid L12

The various mother liquors from the numerous fractions were all worked up until neither free bases nor perchlorates could be crystallized. There was thus obtained a series of resinous products, which were combined and dissolved in dilute hydrochloric acid; the filtered solution was basified, and the bases were extracted with ether. The dried base mixture was distilled *in vacuo* from an air-bath and the fraction boiling at 170 to 180° C. (1 mm.) dissolved in ethyl acetate and neutralized with perchloric acid. The sparingly soluble perchlorate was recrystallized from water and the base obtained from this crystallized from hexane (m.p. 117° C.). It was recrystallized twice more from hexane. Alkaloid L12 as thus obtained consisted of colourless stout prisms melting sharply at 119° C. Found: C, 71.39, 71.14; H, 8.33, 8.34; N, 4.75, 4.69%. Calc. for $C_{18}H_{25}O_3N$: C, 71.29; H, 8.25; N, 4.62%. The perchlorate was recrystallized from acetone-ethyl-acetate. It melted sharply at 244° C. Found: C, 53.06, 52.78; H, 6.92, 6.77; N, 3.53%. Calc. for $C_{18}H_{25}O_3N \cdot HClO_4$: C, 53.53; H, 6.44; N, 3.39%.

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THE THERMAL DECOMPOSITION OF VINYL ETHYL ETHER¹

BY SHENG-NIEN WANG² AND C. A. WINKLER³

Abstract

Over the temperature range 377° to 448° C., vinyl ethyl ether has been found to decompose by a first order reaction to give ethylene and acetaldehyde, at a rate given by

$$k = 4.0 \times 10^{11} e^{-44,400/RT} \text{ sec.}^{-1}.$$

The reaction is capable of sensitizing the decomposition of acetaldehyde and the polymerization of ethylene; this indicates that free radicals are produced during the decomposition of the ether.

Nitric oxide exerts virtually no effect upon the rate of ether decomposition, although it does reduce the rates of pressure change of ether-acetaldehyde mixtures to those corresponding to ether decomposition alone.

It is suggested that the decomposition of vinyl ethyl ether occurs essentially through a rearrangement mechanism, and that free radicals do not play an important part, owing possibly to the inhibiting character of this unsaturated ether.

Introduction

The saturated aliphatic ether series, comprising dimethyl (4, 7), diethyl (2, 3), methyl ethyl (5, 17, 21), and methyl butyl (9) ethers, constitutes one of the relatively few series of organic homologues for which extensive data on the thermal decompositions are available. Less intensive study has been made of methyl propyl (5), dipropyl (16), and di-isopropyl (5) ethers. One investigation of unsaturated divinyl ether has also been made (18). The present paper deals with an investigation of the thermal decomposition of vinyl ethyl ether, undertaken with a view to obtaining further information concerning the relation of structure to the kinetics of such decomposition reactions.

Experimental

A 500 ml. Pyrex reaction vessel, enclosed in an electrically heated furnace, was connected with a capillary mercury manometer, storage bulbs, two Toepler pumps, Bone and Wheeler gas analysis apparatus, nitric oxide generator, traps, McLeod gauge, and vacuum pumps, as in Fig. 1.

Vinyl ethyl ether was prepared by the pyrolysis of acetal (14, 22). The portion of the pyrolytic products distilling below 40° C. was washed twice with concentrated sodium bisulphite solution to remove any aldehyde present, and then twice with water. The material was allowed to stand over calcium chloride for two days, after which it was fractionated very carefully and that portion boiling between 35.3° to 35.5° C. (760 mm.) taken for use. This sample was at once placed in the storage bulb and dissolved air removed by repeated freezing in liquid air and pumping. When not in use, the bulb

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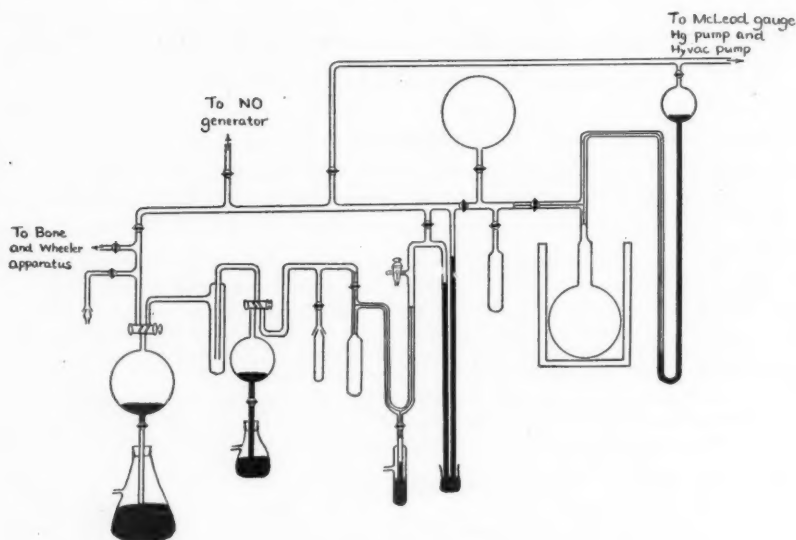


FIG. 1. Apparatus.

was cooled in a dry-ice-acetone bath, since the ether polymerizes quite readily. Even when the ether was preserved in this way, there was formed some polymerized product that separated out as a white flocculent solid when cold. There appeared, however, to be no accompanying change in the rate data.

The reaction was followed by pressure change and analysis. If an analysis was to be made, the reaction mixture was expanded suddenly into the calibrated bulb of one of the Toepler pumps when the desired stage of reaction had been reached, the temperature and pressure of the sample being noted. The sample was then passed back and forth several times through a trap cooled in dry-ice-acetone between the two Toepler pumps to condense unreacted ether and higher boiling products. The total amount of condensable material was determined by transferring it to a calibrated tube, and measuring the pressure at some temperature at which vaporization was complete, a correction being applied for the accompanying residual gas estimated from the pressure when the tube was surrounded with dry-ice-acetone mixture. Aldehyde was determined by the method of Zahorka and Weimann (22). The liquid was transferred into a tube into which 1 ml. of water had been introduced. The aqueous solution so obtained was tested for its acidity, after which 1 ml. of 0.5 *N* sodium sulphite solution was added and the solution allowed to stand for 10 min. It was then titrated with 0.01 *N* hydrochloric acid, using phenolphthalein as indicator. Blank runs showed the method to be satisfactory. The gaseous fraction was analysed in a Bone and Wheeler apparatus.

Results

Normal Decomposition

(1) Analytical Results

Analyses of the uncondensed gases showed the presence of saturated and unsaturated hydrocarbons and carbon monoxide. Hydrogen and acetylene were both found to be absent. A low temperature distillation of accumulated products from several runs, in a column of the Podbielniak type, showed that no "C₃" hydrocarbon fraction was present. The saturated hydrocarbon may therefore be taken as a mixture of methane and ethane, and the unsaturated as ethylene. In Tables I and II, P/P_0 , P_l/P_0 , P_g/P_0 , P_{ald}/P_0 , $P_{C_2H_4}/P_0$, and P_{CO}/P_0 give respectively the ratios, at the time of drawing the sample, of the total pressure, and the partial pressures of total liquid, total gas, aldehyde, ethylene, and carbon monoxide in the reaction mixture to the initial pressure of ether. Among them, values other than those for P/P_0 were obtained by multiplying the respective mole fractions in the reaction mixture by the ratio P/P_0 . The values in parentheses in the last two columns of Table II were obtained from gas compositions interpolated from Table I.

TABLE I
GASEOUS PRODUCTS OF THERMAL DECOMPOSITION OF VINYL ETHYL ETHER

P_0 , cm.	P/P_0	C_2H_4	CO	CH_4	C_2H_6	$CH_4 + C_2H_6$
<i>Temp. 412° C.</i>						
*10±1	1.30	79.4	8.8	7.0	4.9	11.9
†10±2	1.42	73.8	12.7	—	—	13.5
13.4	1.55	66.9	17.4	10.2	5.5	15.7
11.1	1.58	68.4	16.2	9.6	5.8	15.4
15.4	1.62	65.0	14.9	15.0	5.1	20.1
6.6	1.71	63.0	17.4	13.6	5.9	19.5
10.6	1.76	57.4	22.8	13.2	6.6	19.8
13.5	1.78	57.2	21.9	15.6	5.3	20.9
8.6	1.92	52.8	23.5	—	—	23.7
9.9	1.93	49.1	26.9	—	—	24.0
10.5	1.94	51.8	24.2	15.1	8.9	24.0
9.4	2.42	25.6	33.6	29.3	11.5	40.8
<i>Temp. 424° C.</i>						
10.5	1.95	43.4	27.5	—	—	29.1

* The total of four runs was analysed.

† The total of three runs was analysed.

From the results of the gas analyses, it seems evident that, in the main, ethylene is the primary product, while carbon monoxide, methane, and ethane are all secondary products. Extrapolation to zero pressure increase of the plot of ethylene percentage against P/P_0 suggests that in the primary process nearly 93% of the gaseous product is ethylene (Fig. 2). This fact

alone suggests the primary process to be decomposition of ether into ethylene and acetaldehyde. There might be also an unimportant simultaneous process, the existence of which is as difficult to disprove as to confirm. The supposition

TABLE II
PRODUCTS OF DECOMPOSITION OF VINYL ETHYL ETHER
Temp. 412° C.

Time Min. Sec.	P_0 , cm.	P/P_0	P_1/P_0	P_2/P_0	P_{ald}/P_0	PC_2H_4/P_0	P_{CO}/P_0
1 6	9.2	1.20	0.96 ₈	0.23	0.16 ₉	0.19	(0.013)
1 57	9.0	1.28	0.95 ₃	0.33	—	0.24	(0.026)
2 58	9.2	1.43	0.90 ₀	0.53	0.33 ₃	(0.40)	(0.062)
4 38	10.0	1.56	0.88 ₅	0.67	0.39 ₄	(0.47)	(0.10)
6 1	10.0	1.66	0.83 ₅	0.82	0.37 ₄	(0.54)	(0.15)
6 43	10.3	1.68	0.81 ₁	0.87	—	(0.57)	(0.16)
6 49	9.9	1.66	—	—	0.33 ₉	—	—
9 14	11.9	1.77	0.76 ₉	1.00	0.35 ₃	(0.60)	(0.21)
10	10.6	1.77	0.80 ₅	0.96	—	0.55	0.22
13 52	10.6	1.86	0.74 ₉	1.11	0.34 ₂	(0.62)	(0.25)
19 50	9.9	1.93	0.71 ₉	1.21	0.37 ₃	0.60	(0.30)
30 33	10.5	1.94	0.69 ₃	1.25	—	0.65	(0.31)
16Hr.	11.7	2.41	0.27 ₆	2.13	0.10 ₅	(0.59)	(0.68)

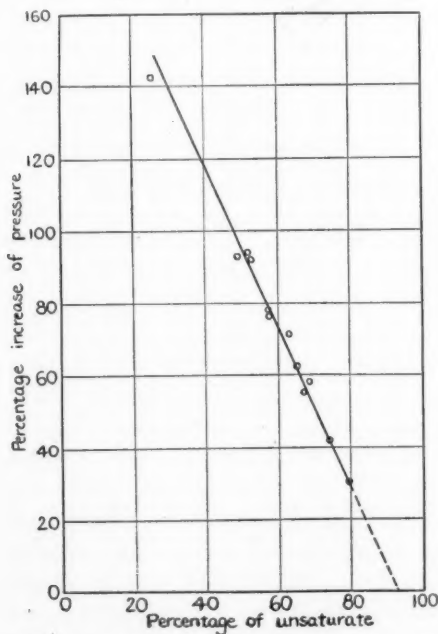


FIG. 2. Relation between pressure increase and amount of unsaturated hydrocarbon in gaseous product. Temperature, 412° C.

of such a primary process is supported by the fact that the relations of $\Delta P/P_0$, P_{ald}/P_0 , and PC_2H_4/P_0 to time of reaction merge into one single curve during the initial period of reaction, as shown in Fig. 3.

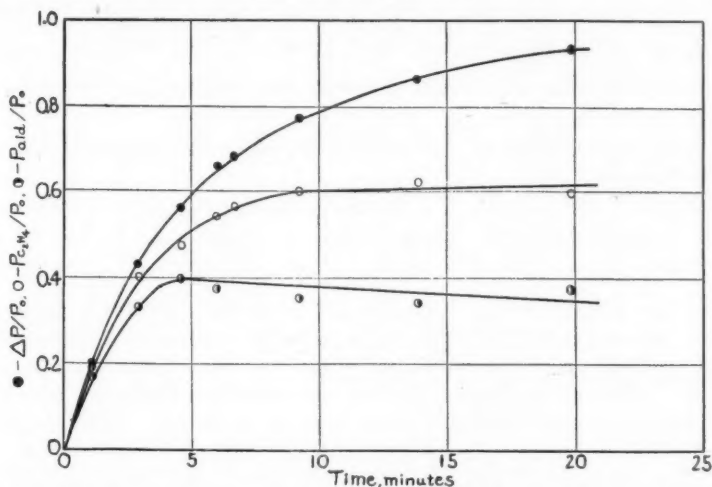


FIG. 3. Relations between pressure increase and changes in amounts of ethylene and acetaldehyde, relative to initial pressure of ether. Temperature, 412 °C.

There are other regularities in the results:

- (1) The amount of methane is always smaller than that of carbon monoxide, while the sum of methane and ethane is approximately equal to the amount of carbon monoxide.
- (2) $(P_{CO} + P_{ald})/P_0$ values are essentially equal to the PC_2H_4/P_0 values during the earlier stages of reaction.

P/P_0	1.20	1.43	1.56	1.66	1.77	1.86	1.93	2.41
PC_2H_4/P_0	0.19	0.40	0.47	0.54	0.60	0.62	0.60	0.59
$P_{CO} + P_{ald}/P_0$	0.18	0.40	0.49	0.52	0.56	0.59	0.67	0.80

The considerable departure in the latter stages may, in part, arise from the sensitized as well as normal polymerization of ethylene as shown to occur in separate experiments with pure ethylene and ethylene-ether mixtures.

- (3) $(PC_2H_4 + P_{CO})/P_0$ values are virtually equal to the corresponding value of $\Delta P/P_0$.

$\Delta P/P_0$	0.20	0.28	0.43	0.56	0.66	0.68	0.77	0.77	0.86	0.93
$(PC_2H_4 + P_{CO})/P_0$	0.20	0.27	0.46	0.57	0.69	0.73	0.81	0.77	0.87	0.90

(4) $(P_{CO} + P_I)/P_0$ values are virtually all equal to unity.

P/P_0	1.20	1.28	1.43	1.56	1.66	1.68	1.77	1.77	1.86	1.93	2.41
$(P_{CO} + P_I)/P_0$	0.98	0.98	0.96	0.99	0.99	0.97	0.98	1.03	1.00	1.02	0.96

It appears that the liquid products are essentially all mono-oxygen compounds.

All these relations can be well accounted for by the following scheme of over-all changes:

- (1) $C_2H_3OC_2H_5 = C_2H_4 + CH_3CHO$ (primary change)
- (2) $CH_3CHO = CH_4 + CO$ (major secondary change)
- (3) $2 CH_3CHO = C_2H_6 + CO + HCHO$ (minor secondary change)

The reaction represented by Equation (3) is merely a tentative suggestion. However, ethane cannot be derived from the ether as a result of its decomposition into ethane and ketene, since no ketene was detectable in the reaction products. It should be emphasized that the equations represent merely the stoichiometric relations among the reactants and products. Nothing can be inferred from the analytical results alone about the real mechanisms through which these changes are effected. As a matter of fact, pure acetaldehyde decomposes at a negligible rate at $412^\circ C.$, as shown by blank experiments, and the change represented in Equation (3) has never been observed in the normal decomposition of acetaldehyde at more elevated temperatures.

(2) Reaction Order and Rate Expression

The rates of pressure change in an empty bulb and in a packed bulb having a surface-volume ratio 10 times that of the empty bulb did not differ appreciably, from which it may be concluded that the reaction is essentially homogeneous.

From the analytical results, it is apparent that only in the initial period of reaction does the percentage pressure change correspond to the percentage ether decomposition. Therefore, in comparing the decomposition rates at different temperatures and different initial pressures, times for 20, 30, and 40% pressure increases are used. The reaction is essentially of the first order, as seen from the typical results in Table III.

From the pressure measurements over the temperature range 377° to $448^\circ C.$, different values of the activation energy and frequency factor were determined for different percentage pressure increases.

Pressure increase, %	Frequency factor, sec. ⁻¹	Activation energy, cal.
20	$4.6 \cdot 10^{11}$	44,600
30	$5.1 \cdot 10^{11}$	44,800
40	$9.1 \cdot 10^{11}$	45,600

TABLE III
TIMES FOR DIFFERENT PERCENTAGE PRESSURE INCREASE OF VINYL ETHYL ETHER
DECOMPOSITION

Temp., °C.	Initial pressure, cm.	$t_{20\%}$, sec.	$t_{30\%}$, sec.	$t_{40\%}$, sec.
389	5.1	265	424	609
389	8.8	268	445	660
389	19.0	264	424	615
412	2.7	95	156	232
412	8.5	85	137	199
412	19.3	83	136	198
424	6.5	47	73	105
424	9.1	48	78	113
424	15.3	46	72	103

On the basis of these data, the rate expression for the pure ether is estimated to be:

$$k = 4.0 \cdot 10^{11} e^{-44,400/RT} \text{ sec}^{-1}.$$

Sensitized Decomposition of Acetaldehyde by Vinyl Ethyl Ether

Rates of pressure change of various mixtures of ether and acetaldehyde were determined. The results are given in Table IV. Owing to the complications in the later stages of reaction, the ratio of pressure increase at the end of 90 sec. to the initial pressure of ether, $(\Delta P/P_e)$, is used as a basis for comparison. The normal decomposition of acetaldehyde at 412° C., which is very slight, has been taken into account.

In Fig. 4, $\Delta P/P_e$ values are plotted against values of P_{ald}/P_e , the ratio between the initial pressures of acetaldehyde and ether. It is seen that although there is some dependence of $\Delta P/P_e$ on the value of the total pressure of the

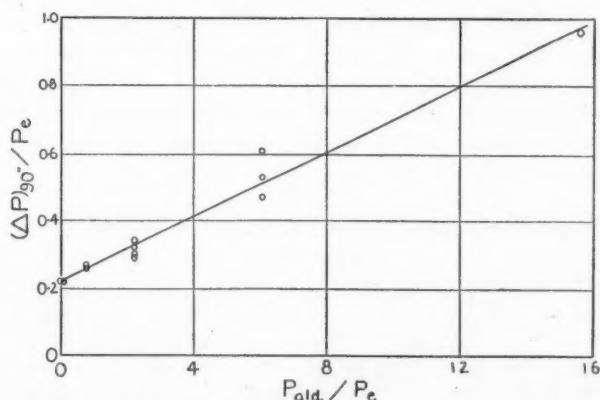


FIG. 4. Relation between ether-acetaldehyde ratio and pressure increase of mixture at end of 90 sec., relative to initial partial pressure of ether.

mixture, the general relation between these two quantities is well represented by a linear expression,

$$\Delta P/P_e = (\Delta P/P_e)_0 + C(P_{ald}/P_e),$$

where $\Delta P/P_e$ and $(\Delta P/P_e)_0$ refer respectively to the pressure increases at the end of 90 sec. relative to the initial pressures of ether for the mixture and for the pure ether, and C is a constant equal to about 0.05.

Consideration of pressure changes after more prolonged reaction times shows that the observed increase in rate is not due to increased decomposition rate of the ether in the presence of acetaldehyde. For example, in the run where P_e is 0.647 cm. and P_{ald} is 10.11 cm., $\Delta P/P_e$ corrected for the normal decomposition of acetaldehyde had the value 4.1 after 30 min. This pressure change cannot logically be assumed to be due to decomposition of ether only. These experiments, therefore, appear to demonstrate quite conclusively that ether molecules produce free radicals during their decomposition which, in turn, induce the decomposition of acetaldehyde.

TABLE IV
SENSITIZED DECOMPOSITION OF ACETALDEHYDE BY VINYL ETHYL ETHER
Temp. 412° C.

P_e , cm.	P_{ald} , cm.	P_{ald}/P_e	$\Delta P/P_e$	P_e , cm.	P_{ald} , cm.	P_{ald}/P_e	$\Delta P/P_e$
8.92	0.0	0.0	0.22	6.36	14.0	2.21	0.34
15.8	1.78	0.11	0.22	0.87	5.27	6.04	0.47
5.72	4.49	0.78	0.26	1.40	8.44	6.04	0.53
11.2	8.82	0.78	0.27	1.98	11.95	6.04	0.61
1.44	3.19	2.21	0.30	0.477	7.45	15.6	0.96
3.33	7.35	2.21	0.32	0.647	10.11	15.6	0.96

Sensitized Polymerization of Ethylene by Vinyl Ethyl Ether

The initial rates for various mixtures of ether and ethylene, as measured by the pressure increase at the end of 90 sec. relative to the initial partial pressure of ether, are summarized in Table V. The results are readily understood by postulating the production of free radicals in the decomposition of the ether. The induced polymerization of ethylene by free radicals would

TABLE V
SENSITIZED POLYMERIZATION OF ETHYLENE BY VINYL ETHYL ETHER
Temp. 412° C.

P_e , cm.	PC_2H_4 , cm.	PC_2H_4/P_e	$\Delta P/P_e$	P_e , cm.	PC_2H_4 , cm.	PC_2H_4/P_e	$\Delta P/P_e$
8.92	0.0	0.0	0.22	7.81	48.2	6.1	0.11
9.24	10.22	1.1	0.20	3.95	47.4	12.0	0.047
9.65	29.6	3.1	0.16	0.72	37.2	52	-0.06

lead to a negative rate of pressure change. This would tend to diminish the rate of total pressure change to an extent increasing with increase in the proportion of ethylene.

Nitric Oxide Inhibition Experiments

Nitric oxide has no appreciable effect on the rate of normal decomposition of vinyl ethyl ether, as shown by the results in Table VI. However, a definite inhibiting effect of nitric oxide on the rate of pressure change in ether-acetaldehyde mixtures was observed. The results are tabulated in Table VII. In both tables, r is defined as the ratio of the pressure increase for the mixture to the pressure increase for pure ether, relative in both cases to the initial pressure of ether in the system, and both taken after 90 sec. reaction time.

TABLE VI

EFFECT OF NITRIC OXIDE ON RATE OF PRESSURE CHANGE FOR THE DECOMPOSITION OF VINYL ETHYL ETHER

Temp., °C.	P_e , cm.	P_{NO} , cm.	r	Temp., °C.	P_e , cm.	P_{NO} , cm.	r
412	8.5	0.0	1.00	412	10.58	0.37	0.98
412	10.23	4.1	1.00	412	5.22	0.32	1.00
412	7.70	3.3	0.94	412	8.84	0.22	1.04
412	10.96	2.1	1.00	389	10.45	1.52	0.99

TABLE VII

EFFECT OF NITRIC OXIDE ON THE RATES OF PRESSURE CHANGE OF VINYL ETHYL ETHER-ACETALDEHYDE MIXTURES

Temp., °C.	P_e , cm.	P_{ald} , cm.	P_{NO} , cm.	P_{ald}/P_e	r
389	1.63	14.7	0	9.0	3.7
389	0.92	8.26	0	9.0	3.3
389	1.03	9.24	0.69	9.0	1.4
389	1.22	10.94	1.55	9.0	0.82
389	1.27	11.45	3.94	9.0	1.1
400	1.69	14.8	0	8.8	4.8
400	1.00	8.8	0.17	8.8	2.9
400	1.17	10.3	1.40	8.8	1.6
400	1.26	11.1	3.56	8.8	1.1
412	1.64	14.8	0	9.0	4.3
412	1.65	14.8	0.25	9.0	2.0
412	1.64	14.7	0.71	9.0	1.2
412	1.51	13.6	1.77	9.0	1.0
412	1.64	14.7	3.70	9.0	1.0
424	1.57	13.8	0	8.8	3.9
424	1.66	14.6	0.19	8.8	2.2
424	1.69	14.8	0.70	8.8	1.7
424	1.97	17.3	1.77	8.8	1.1
424	1.86	16.4	4.05	8.8	0.9

Discussion

The main facts to be considered in attempting to formulate a mechanism for the thermal decomposition of vinyl ethyl ether are: (i) the primary products are essentially ethylene and acetaldehyde; (ii) free radicals capable of sensitizing the decomposition of acetaldehyde and the polymerization of ethylene are produced; (iii) nitric oxide has virtually no effect on the decomposition rate of the pure ether; (iv) nitric oxide does inhibit the reaction in ether-acetaldehyde mixtures.

Some information concerning the free radical producing step can be inferred from the experimental results. In the study of the sensitized decomposition of acetaldehyde in ether-acetaldehyde mixtures, the rate of pressure increase for a mixture containing 6% of ether at 412° C. was found to be about 4.4 times that for pure ether. This means that the length of the chain produced by free radicals from the ether is greatly increased in the presence of acetaldehyde. The chain length in the mixture must, therefore, be smaller than that in pure acetaldehyde. Mitchell and Hinshelwood (10), studying the photolysis of acetaldehyde, found a quantum yield of 338 at 400° C. and 589 at 450° C. both at 100 mm. pressure. At 412° C., it would probably be approximately 400. Gorin (6), studying the same process in the presence of iodine at temperatures around 100° C., found that the decomposition of acetaldehyde into CH_3 and CHO radicals was about three times as probable as the rearrangement into CH_4 and CO . Assuming the same ratio in the present case, the chain length would be around 530. Taking this value as the upper limit of the chain length in the ether-acetaldehyde mixture, the rate of the free radical producing process would be at least $3.4/530$ or 0.6% of the total rate of decomposition. Putting $Ae^{-E/RT}$ as the rate expression for the free radical producing process, the mathematical expression of the above relation would be

$$\frac{4.0 \cdot 10^{11} e^{-44,400/RT}}{Ae^{-E/RT}} \leq \frac{100}{0.6}$$

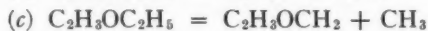
i.e.,

$$\frac{2.4 \cdot 10^{11} e^{(E-44,400)/RT}}{A} \leq 100$$

At 412° C., a difference in activation energy of little more than 6 kcal. corresponds to a 100-fold difference in the exponential factor. Assuming the frequency factor A to be of the order 10^{14} (11), the activation energy can then be, at most, 15 kcal. higher than 44 kcal., i.e., 59 kcal., a quite low value for the activation energy required to break a C—C or C—O bond.

Although it is evident that free radicals are amply produced during the decomposition of vinyl ethyl ether, this does not mean that a major part of the reaction occurs through a chain mechanism. Indeed, from the discussion to follow, it appears that the decomposition of this ether is essentially effected through a rearrangement mechanism.

There are three possible ways in which the ether may split into free radicals, namely,



It is hardly possible to predict the probability of Process (c) relative to (a) or (b), because different kinds of bond splits are involved. For a C—C bond, a single bond in an α -position to a double bond is, in general, stronger, and one in a β -position weaker than a normal single bond (8). If it is assumed that the behaviour of the C—O bond is analogous to that of the C—C bond, Reaction (b) should predominate largely over Reaction (a). In (b) and (c), methyl and ethyl radicals are involved, both of which have been shown capable of reacting with nitric oxide (14, 20).

If free radicals played an important part in the normal decomposition of the ether, nitric oxide would be expected to decrease the rate to an appreciable extent by combining with methyl and ethyl groups formed initially before they could react further, and also by inhibiting the chain propagating process. In the present experiments, however, nitric oxide was found to exert almost no effect over a wide range of ether-nitric-oxide concentration ratios. This can scarcely be attributed to compensation of its catalytic and inhibiting effects, and it must be concluded that nitric oxide exerts neither catalytic nor inhibiting effect on the normal vinyl ethyl ether decomposition. Hence, a chain mechanism apparently does not play an important part in this reaction.

The results for the sensitized decomposition of acetaldehyde and its inhibition by nitric oxide provide further evidence that a chain mechanism does not play an important part in the normal decomposition of vinyl ethyl ether. If it is assumed that free radicals generated from the ether may propagate a chain, they would presumably do so by reacting with either ether or acetaldehyde molecules as follows:



An individual chain propagating through the mixture would be a mixed sequence of these two different types of chains. Therefore, even if it is assumed that nitric oxide has little or no effect on C_2H_5 and $\text{C}_2\text{H}_5\text{OC}_2\text{H}_4$ radicals, it should reduce the chain length in the mixture to not more than a few steps as a result of its inhibiting action with methyl radicals. The minimum value of the nitric oxide inhibited rate of the ether-acetaldehyde mixture should then correspond to the rate of the rearrangement process in the case of the pure ether. The experimental results show that the fully inhibited rate is, in fact, very close to the rate of decomposition of ether alone in all cases studied. Hence, any chain mechanism must play only a minor role in the

normal ether decomposition, and the predominant part of the reaction proceed through a rearrangement mechanism.

Since the chain initiating processes are quite frequent (more than 0.6% of the total rate), but the chain reaction does not play an important part, the chains must be very short. For the chains to be very short, either the chain propagating steps involve high activation energies comparatively, or vinyl ethyl ether is itself very efficient in associating with free radicals to deactivate them. It is impossible to say anything definite about the activation energies of the chain propagating steps. On the other hand, it is by no means unexpected that this ether, like ethylene (1), propylene (12), and azomethane (19) should be able to inhibit chain propagation as a result of its unsaturated linkage.

Assuming that the chain mechanism plays only a small part in the normal decomposition of vinyl ethyl ether, it is possible to account for the approximate quantitative relation found in the sensitized decomposition of acetaldehyde at 412° C., and previously expressed by

$$\Delta P/P_e = (\Delta P/P_e)_0 + C(P_{ald}/P_e).$$

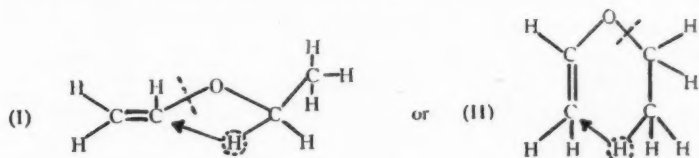
Equating $\Delta P/\Delta t$ at the end of 90 sec. to the initial rates, and putting it in another form, the relation becomes:

$$\text{Rate of pressure increase of mixture} = (\text{rate of pressure increase of pure ether at the same pressure as the partial pressure of ether in the mixture}) + C' (\text{pressure of acetaldehyde}),$$

where C' is $4.5 \cdot 10^{-4} \text{ sec.}^{-1}$. Assuming that the rate of pressure increase for pure ether is equal to the rate of the rearrangement process, the rate of pressure increase for the mixture minus the rate of pressure increase for pure ether gives the rate of pressure increase due to the sensitized decomposition of acetaldehyde. The rate of sensitized decomposition is then seen to be directly proportional to the acetaldehyde concentration, but independent of the ether concentration over the range studied. The proportionality of this rate to the acetaldehyde concentration is readily understood. The chain length in pure acetaldehyde is much greater than in vinyl ethyl ether, as discussed previously. Therefore, for the mixture the effect of acetaldehyde on the chain ending process may be neglected. Moreover, since acetaldehyde does not start chains nor lead to any chain branching process, the introduction of acetaldehyde would not affect the concentration of free radicals to a large extent. The rate of the sensitized decomposition, being proportional to the product of the acetaldehyde concentration and free radical concentration, would be therefore proportional to the concentration of acetaldehyde or its partial pressure in the mixture. The fact that the rate of sensitized acetaldehyde decomposition is nearly independent of the pressure of ether implies that, to a first approximation, the free radical concentration produced by vinyl ethyl ether during its decomposition is a constant value, independent of the pressure of the ether, at least in the pressure range studied. Since the rate of the free radical producing process is presumably directly proportional

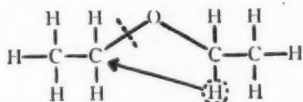
to the pressure of ether, this relation further indicates that the rate of removal of free radicals is also directly proportional to the pressure of the ether.

The decomposition of vinyl ethyl ether by a rearrangement process could conceivably occur in either of the following ways:



Mechanisms of the type represented by (II) have been suggested previously (13) for several thermal decomposition reactions.

A type (I) mechanism for the vinyl ethyl ether rearrangement gains support, however, if comparison is made with the decomposition of diethyl ether, inhibited by nitric oxide, where the rearrangement is to be represented, presumably, by:



The difference in the activation energies of the rearrangement processes for the two ethers may be ascribed to two main factors. First, the shielding effect of the bonds surrounding the carbon atom being attacked is greater in diethyl ether than in vinyl ethyl ether. Secondly, the higher electron density around the unsaturated carbon atom in vinyl ethyl ether would facilitate approach of the migrating hydrogen atom. This latter factor, being a van der Waal energy term, amounts to perhaps a few kilocalories. As to the shielding effect, Rice and Teller (13) estimate the energy required to push the three hydrogen atoms of methane symmetrically into the same plane as the carbon atom to be around 40 kcal. This is taken by these authors as the contribution to the activation energy of the shielding effect in the exchange reaction



If the difference of the shielding effects for the rearrangement processes of the two ethers is assumed approximately equal to the effect due to one hydrogen atom in the hydrogen-methane exchange reaction, the difference in activation energy arising from this cause would be around 13 kcal. By adding these two effects together, the difference between the activation energies for the rearrangement processes of these two ethers might amount to 15 to 20 kcal. The estimated value for the activation energy of the vinyl ethyl ether rearrangement would be of the order 42 to 47 kcal., to be compared with the measured value of 44 kcal. Hence, there seems to be justification for assuming that rearrangement of vinyl ethyl ether is by the Type I mechanism indicated previously.

It has been pointed out before that the rearrangement process leading to the formation of ketene and ethane from vinyl ethyl ether is entirely absent. This is to be expected since such a process would require even higher activation energy than that for the rearrangement process of a saturated ether, owing to the fact that the hydrogen atom of a vinyl group is more firmly bound to the carbon atom than the hydrogen atom of an alkyl group. The same reason may also account for the fact that the rearrangement process of divinyl ether into ethylene and ketene involves at least 50 kcal. (18), while the value for the rearrangement of vinyl ethyl ether is only 44 kcal.

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